

Structural flexibility of cuprate superconductors

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We study the lowest energy state in the CuO_2 plane of cuprate superconductors, related to the vibration that does not involve distortions of constituent units of the plane, the Rigid Unit Mode (RUM). We discuss the correlated motion in the plane due to RUM on temperature decrease, and possible relevance of this phonon for superconductivity.

The existence of the hierarchy of interatomic interactions in a solid can make a substantial reduction in analyzing its properties. If the energy to break a chemical bond between two atoms considerably exceeds the thermal energy, such a bond can be viewed as a Lagrangian constraint, in a sense that it keeps two atoms at a fixed distance. This idea can be made useful in the case of covalent materials, in which two-body stretching and three-body bending forces considerably exceed all others. These short-range interactions can be translated into the building blocks of a mechanical network. This has been the starting point of the Phillips theory of network glasses [1]. By requiring that the number of degrees of freedom is equal to the average number of bonding constraints, this theory predicted the average coordination number of $\langle r \rangle = 2.4$ for which glass forming ability is optimized. Since then, this picture has been widely used to discuss relaxation in covalent glasses and crystals.

The constraint theory offers a great reduction in treating the interactions in a solid, by translating static, vibrational and relaxation properties of a solid into those of a mechanical network, with well-developed methods to study it. For example, the procedure known as Maxwell counting can make rigorous predictions about the low-energy states of the system. Any modes in a mechanical network that keep local constraints (e. g. two-body stretching and three-body bending constraints) intact, have zero frequency because there is no restoring forces to such deformations. According to Maxwell counting, the number of such modes is equal to the difference between the number of degrees of freedom, N_f , and the number of bonding constraints, N_c . Therefore, the existence of the hierarchy of interactions in a solid can have important implications for the hierarchy of vibrational modes in terms of their frequency. In the simulation study of constraint counting in glasses, “floppy” modes appear when the network becomes under-constrained, $N_c < N_f$, or $\langle r \rangle < 2.4$ [2] (the term “floppy” here points to the fact that in real systems, weaker interactions always give a non-zero restoring force associated with propagation of constraint-obeying modes, making their frequency not zero exactly, but some small values).

By construction, the picture which maps interatomic interactions into a network of mechanical constraints, is limited to solids with short-range covalent interactions. If ionic contribution to bonding is substantial, the map-

ping of interatomic interactions into a network is problematic due to the long-range nature of Coulomb forces and the absence of the hierarchy of interactions [3]. It is nevertheless still possible to consider many important properties of solids with substantial ionic contribution to bonding, using a very general idea that a certain chemical interaction can be mapped into a mechanical constraint. Consider very common silica glass. Ionic contribution to Si-O bond is at least as strong as covalent one, resulting in the fact that although O-Si-O bending constraint is intact, Si-O-Si angular constraint is broken, as is seen by the very broad distribution of Si-O-Si angles [4]. Hence the usual constraint counting procedure would overestimate rigidity of silica glass. However, despite the substantial ionicity of Si-O bond, it is known from both experiments and computer simulations that SiO_4 tetrahedra are very rigid. This is related to the high energy cost involved in the deformation of the electronic density that has a tetrahedral symmetry. Hence if we are interested in low-energy vibrations of silica, its Phillips network analogue is a collection of SiO_4 rigid units, loosely connected at corners. Thus even though there is a considerable ionic contribution to bonding in a solid, the knowledge of its structure and chemistry can still allow us to map interatomic interactions into a generalized network, albeit with different building blocks: these do not correspond to two- and three-body constraints as in the Phillips theory, but to local rigid units. The modes that propagate in without its constituent units having to distort have been named Rigid Unit Modes (RUMs) [5].

In this paper, we discuss the ability of cuprate high-temperature superconductors to support the RUM, which we associate with the lowest non-trivial energy state in CuO_2 plane. A distinct property of the RUM is its infinite (in the idealized model) correlation length. We discuss the behaviour of the RUM on temperature decrease, and its possible relevance for superconductivity.

We consider the common structural unit of cuprate superconductors, the CuO_2 plane. In order to discuss the ability of this system to support RUMs, one needs to identify rigid units, analogous to SiO_4 tetrahedra in silica. Cuprate superconductors are materials with mixed covalent and ionic bonding, hence, unlike in silica, their structures do not immediately offer the way to map them into the collection of rigid units, which reflects the bond-

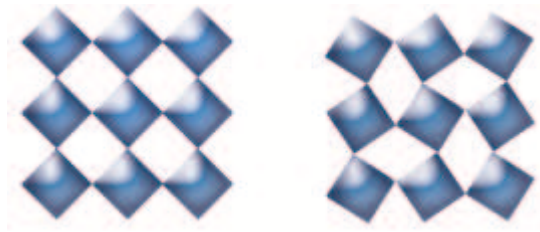


FIG. 1: The Rigid Unit Mode (RUM) in the CuO_2 plane of cuprate superconductors.

ing type. A useful insight comes from the experimental and quantum-mechanical results that there is substantial covalency in Cu–O bonding in the Cu–O plane [6]. Next, as in silicates, experiments point to the broken O bond-bending constraints [7]. This allows us to consider the two-dimensional system of corner-shared rigid CuO_4 squares, loosely connected at corners (compare to a silicate, modeled in the RUM model as the system of rigid SiO_4 units, loosely connected at corners).

For this system, Maxwell counting gives the result that it is over-constrained, $N_c > N_f$. Indeed, each square has three degrees of freedom in the plane, two translational and one rotational, giving $N_f = 3$. There are two constraints per shared corner, or one constraint per corner per CuO_4 unit, or 4 constraints per unit in total, $N_c = 4$. Hence Maxwell counting predicts that no RUM-type distortions should exist in CuO_2 plane. However, this approach does not take into account the important property of the system, its symmetry. It has been realized that symmetry can make certain constraints redundant, resulting in the effective increase of system flexibility against RUMs. This can be studied in some detail using the lattice dynamics approach to analyze the flexibility of a system of connected rigid units, loosely connected at corners. This method rigorously finds all RUMs in a given system, in addition to three trivial acoustic modes at $k = 0$ [5]. For the perovskite system, it has been shown that symmetry reduces the number of constraints in such a way as to give one particular RUM that corresponds to rotations and displacements of rigid units [8].

We can readily extrapolate this result to the two-dimensional analogue of the perovskite structure, the system of connected CuO_4 squares. The corresponding mode, the optic RUM, is shown in Figure 1.

It is interesting to note that negative thermal expansion, decrease of volume (or some of the system's linear dimensions) on temperature increase, is a clear signature of the presence of RUMs in a system. Indeed, distortion shown in Figure 1 pulls the structure onto itself, and if this effect exceeds thermal expansion, the net effect can be volume reduction on temperature increase. Using this picture, it has been possible to explain negative thermal expansion in a variety of RUM-floppy materials [9]. This

effect is also seen in the in several cuprates as anomalous change of the unit cell parameters in CuO_2 plane. For example, in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, deviation from the linear decrease of the parameters of CuO_2 plane is seen around superconducting temperature T_c , followed by the negative thermal expansion at lower temperature [10]. We can therefore interpret these effects as the manifestation of existence of the RUM in the CuO_2 plane.

That cuprate superconductors can support the mode shown in Figure 1 (referred to as the RUM in the discussion below) is not a new result. What is important, however, is the method of its derivation, from developing the idea about the hierarchy of interactions in the solid into the algorithm that rigorously finds all RUMs in a given system. By this construction, the RUM is the lowest energy vibrational state in the CuO_2 plane (apart from trivial acoustic modes), because it does not involve bond-stretching and bond-bending distortions that come at high energy cost. Any other non-trivial in-plane mode has necessarily higher frequency because it involves bending and stretching bonds (for example, the energy of the bond-stretching breathing mode is 18–20 THz [11], several times larger than the RUM frequency, see below). This has implications for the low-energy correlated motion in the CuO_2 plane, as we discuss below.

An important feature of the RUM shown in Figure 1 concerns its correlation length ζ , which enters the coordinate correlation function $\langle q(\mathbf{r})q(0) \rangle \propto \exp(-r/\zeta)$. In the model in which CuO_4 squares are rigid, $\zeta = \infty$, reflecting the fact that rotation of one square necessarily triggers the motion (rotations and displacements) of squares in the whole plane (see Figure 1). To appreciate this property, it is instructive to consider two different types of systems for which this is not the case. An example of the first type is the system in which triangles, as opposed to squares, are loosely connected at corners to form the network of six-member rings. The RUM model, applied to this system, gives the result that unlike the system of connected squares, there are many of ways in which such a system can distort by local *independent* RUMs. In other words, the connected system of triangles is much more RUM-floppy than that of the squares. This can be understood using the Maxwell counting discussed above: the number of degrees of freedom for the system of triangles is the same as for the square system, $N_f = 3$ per unit, but the number of constraints per unit, $N_c = (3 \cdot 2)/2 = 3$, is smaller than that for the square system ($N_c = 4$). As a result, the correlation length is limited to several unit cells only: it is easy to show that for the system of connected triangles, rotation of one triangle involves rotations and displacements of triangles within the radius of 2-3 ring diameters only. Another example of a system of the first type is the three-dimensional random network of tetrahedra, loosely connected at corners. Similar to the previous example, the RUM model gives the result that there are many ways in which this system can distort

by independent RUMs [14]. As a result, the correlation length ζ is only about 10 Å, as deduced from the neutron scattering experiments [15]. The second type of systems are very different from the first type: they do not support RUM at all. The structure of silicon is one such example. Here, unlike in SiO₂, all bending constraints are intact, and the structure is severely over-coordinated to allow for existence of any RUMs.

From the topological point of view, one can therefore view the two-dimensional system of connected squares in Figure 1 as an interesting borderline and, perhaps, unique, case for its ability to support low-energy vibrations. It is neither under-constrained as to give many RUMs and hence small correlation length, nor over-constrained as to inhibit RUMs altogether. The balance of the degrees of freedom and the number of constraints, together with the system's symmetry, give the result that only one single RUM is present (see Figure 1), which has the infinite correlation length. It should be noted that $\zeta = \infty$ is true only in the model in which the CuO₄ units are infinitely rigid. In practice, there is always a finite distortion of the units, leading to a finite ζ which, however, considerably exceeds the size of the unit. In this case, on temperature decrease (see below), the correlated atomic motion in the plane takes place in the domains of size ζ . Generally, ζ can be affected by the multitude of interactions present in the cuprate system at low temperature.

The frequency of the RUM mode is zero only in the RUM model, and in real cuprates, ν_r is defined by the inter-unit and other next-order interactions, as well as by the effects of steric hindrance on the CuO₂ plane. During the rhombic distortion, one pair of O atoms comes closer to the out-of-plane cations directly above the rhomb centre (for example, in La₂CuO₄, these are La/Sr ions; in YBa₂Cu₃O₇, these are Y and Ba ions), whereas the remaining pair comes closer to the cations above the centres of neighbouring rhombs. The energy of these interactions sets the scale of ν_r .

A large body of data exists on phonons in cuprates. Most of the recent discussion has concentrated on the higher-energy breathing and half-breathing modes, whereas the RUM is not commonly discussed. A possible reason for this is that this low-frequency mode is hardly visible in the total density of states [12]. In earlier studies [11, 13], the combination of neutron scattering experiments with lattice dynamics calculations has identified the RUM as the zone boundary optic phonon with ν_r in the 3–3.6 THz range in the tetragonal phase of Nd₂CuO₄, Pr₂CuO₄, La₂CuO₄, and 6.3 THz in YBCO.

We can now discuss the vibrational behaviour in the CuO₂ plane as temperature decreases. We first note that the values of ν_r above are considerably higher than in other RUM-floppy systems (for example, in silicates, ν_r is in the range 0–1 THz [12]). One can therefore expect that temperature T_r , at which transition of the

RUM to the ground state takes place, is relatively high. T_r can be calculated from the order-of-magnitude estimation that the temperature-dependent term in the RUM energy, $\langle E_r \rangle = \frac{1}{2}h\nu_r + h\nu_r/(\exp(h\nu_r/kT) - 1)$, is ten times smaller than the ground state energy, giving $\exp(h\nu_r/kT) - 1 = 20$ and $kT_r = 0.33h\nu_r$. Taking ν_r from the 3–6.3 THz range above, we obtain T_r in the 48–101 K range, and we remark here that T_r is on the scale of T_c of cuprate superconductors. An approximate estimate for the vibrational amplitude q in the RUM ground state gives a relatively large value, $q = (h/2m\nu_r)^{1/2} = 0.18\text{--}0.26$ Å, if m is the mass of the CuO₄ unit.

At high temperature $T > T_r$, atomic motion in the plane is the superimposition of all phonons in their excited states. Although the RUM is present, the atomic displacements are de-correlated by other high-energy phonons with small correlation lengths. By construction, the RUM is the lowest energy state in the CuO₂ plane, apart from the acoustic modes. Therefore at T_r , all the phonons in the higher-frequency optic branches freeze in their ground states. These phonons, with the upper frequency of about 22 THz, constitute the majority of vibrations in the cuprate density of states [11]. At T_r , de-correlation effects due to these phonons are decreased due to the reduced vibrational amplitudes in their ground states, which, for higher-frequency phonons, are further reduced as $\langle q^2 \rangle \propto 1/\nu$. As a result, the correlated motion on lengthscale ζ , set by the RUM (dominant in terms of the vibrational amplitude), increases. In this respect, it is interesting to recall the ion channeling experiments in several cuprates, which showed that the atomic motion becomes highly correlated at the superconducting transition [16]. It should be noted that at T_r , low-frequency acoustic phonons remain to be in their excited states; however, as we discuss below, de-correlation effects at long wavelengths may not be important.

We now discuss possible relationship between the RUM, T_r and superconductivity. First, coupling between charge carriers and the RUM is expected to be large. In BSCCO, for example, the spectral function shows strong coupling to modes in the 12–27 meV range [17] ($\approx 3\text{--}6$ THz), which is close to the range of ν_r . Second, one can tentatively discuss how the RUM is related to the phase coherence between the charge carriers (e.g., Cooper pairs). Suppose a pair is formed as the result of an electron (hole) scattering the RUM phonon at, for example, O site, and another electron absorbing it at a distance ξ . If, at the same time, another pair is formed in the same way in a different region of the plane, but within the distance ζ from the first pair, the two pairing events are identical due to the correlated RUM motion (see Figure 1), resulting in the correlation between the phases of the pairs. In this sense, the RUM has no bearing on the coherence of the Cooper pairs if $\xi \ll \lambda$, as in the case of ξ for cuprates and λ for long-wavelength acoustic phonons. An interesting observation is that in cuprates, the size of

the Cooper pair, ξ (13 Å in YBCO [18]), is comparable with the RUM modulation length, $\lambda_r \approx 2\sqrt{2}d \approx 11$ Å, where d is the O-O distance (see Figure 1).

The relationship between the RUM, T_r and superconductivity discussed above needs further study. However, if this relationship exists, it is consistent with several broad experimental correlations. First, one expects that T_c should be maximized in the system in which the RUM is favoured most. Experimentally, for different cuprates at a given doping level, T_c is maximal in structures in which the CuO₂ plane is flat and square [18]. In our picture, this behaviour can be rationalized by noting that the RUM is most favoured when the CuO₂ plane is as close to being flat and square as possible. On the other hand, distortion of the plane results in suppression of the RUM (see Figure 1). The distortion can be plane buckling due to either static or dynamic tilting motion. In this case, suppression of the RUM is caused by the out-of-plane strains, although these can be partially compensated by slightly different Cu-O distances [19]. Another type of distortion can be the rhombic distortion of the flat plane, which also suppresses the RUM due to the lower symmetry of the orthorhombic phase relative to the tetragonal one. Second, one expects that T_c should increase with ν_r , since a larger ν_r implies a higher temperature of the onset of correlated motion, $T_r \propto \nu_r$. Experimentally, cuprates show unconventional relationship between T_c and lattice stiffness: unlike in strongly coupled BCS superconductors, in cuprates, T_c increases with lattice stiffness, or Debye temperature, within a given cuprate group [18]. In our picture, this behaviour can be rationalized by noting that ν_r (and hence T_r) increases with lattice stiffness. Third, pressure, stiffening the lattice, increases ν_r . In our picture, this should result in the increase of T_c , and is consistent with experimental data. Fourth, one expects to find a positive isotope shift due to atoms involved in the RUM motion, i.e. in-plane atoms. This is consistent with experiments that show that the predominant contribution to the (positive) isotope shift comes from the planar atoms [20]. It is also found that the isotope shift decreases with T_c [20]. In this respect, it is interesting to note that a smaller atom mass, in addition to increasing T_c (giving the positive isotope shift $T_c \propto 1/m^\alpha$), also increases $\langle q^2 \rangle \propto 1/m\nu \propto 1/\sqrt{m}$, therefore increasing de-correlation effects of higher-energy phonons. In our picture, this decreases T_c , and this effect is expected to be more pronounced at higher temperatures.

Finally, it is interesting to note that in cuprates, the charge in the CuO₂ plane is dynamically ordered in stripes that run either along Cu-Cu-Cu or Cu-O-Cu bonds [18]. This pattern is consistent with the field of the RUM displacements (see Figure 1). This hints to a possible relationship between the RUM-induced field and the dynamic stripe order. This picture may be the sub-

ject of further study that also includes other interactions (e.g., magnetic) present in the system.

In summary, we discussed the property of cuprate superconductors to support modes that do not involve distortions of constituent units. The corresponding mode, the RUM, is the lowest non-trivial energy state in the CuO₂ plane. We discussed the correlated motion in the plane due to RUM on temperature decrease, and possible relevance of this phonon for superconductivity.

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